

Flexoelectric effect modeling

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Abstract

The statistical theory of the dipole flexoelectric (FE) polarization in liquid crystals is used to calculate the temperature dependence of order parameters, the elastic constants and the FE coefficients. Two systems with polar wedge-shaped and banana-shaped molecules are investigated. In both cases the FE coefficients are proportional to the dipole moment component parallel to the molecule symmetry axis. The origin of the FE effect and microscopic pictures of the distorted phases are discussed.

Keywords: nematic liquid crystals, flexoelectric polarization, elastic constants, statistical theory.

1 Introduction

In an ideal nematic liquid crystal the molecules are on average aligned along one common direction $\pm\vec{N}$ [1]. There is usually some deformation of the alignment and the vector \vec{N} depends on the position \vec{r} in the liquid crystal. The free-energy density due to the distortion of the vector \vec{N} is expressed in terms of the vector derivatives and the elastic constants K_i [2]

$$f_d = \frac{1}{2}K_1(\nabla \cdot \vec{N})^2 + \frac{1}{2}K_2[\vec{N} \cdot (\nabla \times \vec{N})]^2 + \frac{1}{2}K_3[\vec{N} \times (\nabla \times \vec{N})]^2, \quad (1)$$

where K_1 , K_2 , and K_3 are splay, twist, and bend elastic constants, respectively.

In a deformed uniaxial nematic liquid crystal, there should appear in many cases a spontaneous dielectric polarization invented by Meyer [3]

$$\begin{aligned}\vec{P} &= e_1 \vec{N}(\nabla \cdot \vec{N}) + e_3(\vec{N} \cdot \nabla) \vec{N} \\ &= e_1 \vec{N}(\nabla \cdot \vec{N}) - e_3 \vec{N} \times (\nabla \times \vec{N}),\end{aligned}\tag{2}$$

where e_1 and e_3 are the splay and the bend flexoelectric (FE) coefficients, respectively. The appearance of the spontaneous polarization in liquid crystals as a result of orientational deformations is called the flexoelectric effect.

The FE coefficients and the elastic constants are macroscopic parameters that are important in practical applications of liquid crystals. Thus, it is interesting to study the connection between microscopic and macroscopic parameters in order to facilitate new material production. In this paper we will focus on the FE effect.

A microscopic mechanism of the FE effect was proposed by Meyer [3], who showed that it is a steric effect due to the asymmetry of the molecular shape. But Prost and Marcerou [4] noticed that the polarization in a deformed liquid crystal can be also produced as a result of a gradient in the average density of quadrupole molecule moments. In 1976 Straley developed a microscopic theory [5] by extending the Onsager theory of orientational ordering in hard-rod gases. Other mean-field theory was given by Derzhanski and Petrov [6]. The density-functional theory was derived by Singh and Singh [7], where the dipole and the quadrupole contributions to the FE coefficients were taken into account. Somoza and Tarazona [8] tried to include the effects of the relaxation in the angular distribution function of the deformed nematic. As far as computer simulations are concerned, we would like to mention the papers by Stelzer *et al.* [9] and by Billeter and Pelcovits [10], where pear-shaped molecules were studied.

In this paper, we present two systems with wedge-shaped and banana-shaped molecules. In our calculations, we use a simple potential energy of interactions which allows us to obtain the macroscopic parameters of the systems and to understand the FE effect origin in the deformed phases.

2 Expressions for flexoelectric coefficients

The microscopic free energy for the system can be derived in the thermodynamic limit ($N \rightarrow \infty$, $V \rightarrow \infty$, $N/V = \text{const}$) from the Born-Bogoliubov-Green-Kirkwood-Yvon (BBGKY) hierarchy [11] or as the cluster expansion

for the uniaxial systems [12]. The total free energy F consists of the entropy term and the interaction term, namely

$$F = F_{ent} + F_{int}, \quad (3)$$

where

$$\beta F_{ent} = \int d\vec{r} dR G(\vec{r}, R) \{\ln[G(\vec{r}, R)\Lambda] - 1\}, \quad (4)$$

$$\beta F_{int} = -\frac{1}{2} \int d\vec{r}_1 dR_1 d\vec{r}_2 dR_2 G(\vec{r}_1, R_1) G(\vec{r}_2, R_2) f_{12}. \quad (5)$$

Here $f_{12} = \exp(-\beta\Phi_{12}) - 1$ is the Mayer function, Φ_{12} is the potential energy of interactions, $dR = d\phi d\theta \sin\theta d\psi$, $\beta = 1/(k_B T)$, and Λ is related to the ideal gas properties. The normalization of the one-particle distribution function G is

$$\int d\vec{r} dR G(\vec{r}, R) = N. \quad (6)$$

The equilibrium distribution G minimizing the free energy of Eq. (3) satisfies the equation

$$\ln[G(\vec{r}_1, R_1)\Lambda] - \int d\vec{r}_2 dR_2 G(\vec{r}_2, R_2) f_{12} = \text{const.} \quad (7)$$

In the case of the homogeneous uniaxial nematic phase, the distribution function depends only on the molecule orientation $G(\vec{r}, R) = G_0(R)$. We will further assume that G depends on a single argument $G_0(R) = G_0(\vec{n} \cdot \vec{N})$, where \vec{N} determines the phase orientation. This is satisfied exactly for the molecules with $C_{\infty v}$ symmetry but we expect that it is plausible for the banana-shaped molecules with C_{2v} symmetry. The molecule electric dipole moment is defined as

$$\vec{\mu} = \mu_1 \vec{l} + \mu_2 \vec{m} + \mu_3 \vec{n}, \quad (8)$$

where the unit vectors $(\vec{l}, \vec{m}, \vec{n})$ describe the molecule orientation.

In the case of the wedge-shaped molecules, the FE coefficients have the form [13]

$$e_1 = \mu_3 \int d\vec{u} dR_1 dR_2 f_{12} G_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_x n_{1z} n_{2x}, \quad (9)$$

$$e_3 = \mu_3 \int d\vec{u} dR_1 dR_2 f_{12} G_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_z n_{1x} n_{2x}, \quad (10)$$

where \vec{n} determines the molecule $C_{\infty v}$ symmetry axis. In the case of the banana-shaped molecules, the FE coefficients can be written in the approximated form provided that \vec{l} determines the molecule C_{2v} symmetry axis and \vec{n} determines the long molecule axis [14]

$$e_1 = \mu_1 \int d\vec{u} dR_1 dR_2 f_{12} G_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_x l_{1z} n_{2x}, \quad (11)$$

$$e_3 = \mu_1 \int d\vec{u} dR_1 dR_2 f_{12} G_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_z l_{1x} n_{2x}. \quad (12)$$

In both cases, the FE coefficients are proportional to the dipole moment component parallel to the molecule symmetry axis. It results from the symmetries of the interactions and of the Mayer function. The elastic constants of the uniaxial nematic phase are [15]

$$\beta K_1 = \frac{1}{2} \int d\vec{u} dR_1 dR_2 f_{12} G'_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_x^2 n_{1x} n_{2x}, \quad (13)$$

$$\beta K_2 = \frac{1}{2} \int d\vec{u} dR_1 dR_2 f_{12} G'_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_y^2 n_{1x} n_{2x}, \quad (14)$$

$$\beta K_3 = \frac{1}{2} \int d\vec{u} dR_1 dR_2 f_{12} G'_0(\vec{n}_1 \cdot \vec{N}) G'_0(\vec{n}_2 \cdot \vec{N}) u_z^2 n_{1x} n_{2x}. \quad (15)$$

3 Results

The calculations were performed for the square-well potential energy of the form

$$\Phi_{12}(u/\sigma) = \begin{cases} +\infty & \text{for } (u/\sigma) < 1, \\ -\epsilon & \text{for } 1 < (u/\sigma) < 2, \\ 0 & \text{for } (u/\sigma) > 2, \end{cases} \quad (16)$$

where u is the distance between molecules, $\vec{r}_2 - \vec{r}_1 = u\vec{\Delta}$, and σ depends on the molecule orientations and on the vector $\vec{\Delta}$. For σ , we used simple expressions with three parameters, σ_0 defines the length scale, σ_1 defines the nematic term, and σ_2 defines the FE term. In the case of the wedge-shaped molecules σ has the form

$$\sigma = \sigma_0 + \sigma_1 [(\vec{\Delta} \cdot \vec{n}_1)^2 + (\vec{\Delta} \cdot \vec{n}_2)^2] + \sigma_2 (\vec{\Delta} \cdot \vec{n}_1 - \vec{\Delta} \cdot \vec{n}_2), \quad (17)$$

whereas for the banana-shaped molecules

$$\sigma = \sigma_0 + \sigma_1 [(\vec{\Delta} \cdot \vec{n}_1)^2 + (\vec{\Delta} \cdot \vec{n}_2)^2] + \sigma_2 (\vec{\Delta} \cdot \vec{l}_1 - \vec{\Delta} \cdot \vec{l}_2). \quad (18)$$

We used the density $NV_{mol}/V = 0.1$, $\sigma_1 = 2\sigma_0$, $\sigma_2 = \sigma_0$. The molecule volume V_{mol} was estimated from the mutually excluded volume. The FE coefficients were expressed in μ_i/σ_0^2 , the elastic constants in ϵ/σ_0 , and the temperature in ϵ/k_B . The potential energy of the form $\Phi_{12}(u/\sigma)$ allows us to express the FE coefficients and the elastic constants as a finite series of the order parameters where the coefficients of the expansion can be calculated analitically. As a consequence it is easy to change the set of parameters σ_i and to study different systems.

The temperature dependence of the order parameters and the elastic constants is similar to the known results [13], therefore the FE coefficients will be discussed only.

3.1 Wedge-shaped molecules

In the system of the wedge-shaped molecules, on decreasing the temperature we meet the first order transition from the isotropic to the uniaxial nematic phase at $T_C = 0.7287$. The temperature dependence of the FE coefficients is presented in Fig. 1. The physical picture is shown in Fig. 2. On decreasing the temperature, the bend coefficient e_3 is almost constant while the splay coefficient e_1 increases monotonically. The wedge-shaped molecules fit to the splayed structure and there is an excess of molecules pointing to the splay origin. The induced polarization has the opposite direction. In the bend structure the FE polarization points to the bend centre because the molecules are slightly turned in the opposite direction.

3.2 Banana-shaped molecules

In the system of the banana-shaped molecules, on decreasing the temperature we meet the first order transition from the isotropic to the uniaxial nematic phase at $T_C = 0.6611$. The temperature dependence of the FE coefficients is presented in Fig. 3. The physical picture is shown in Fig. 4. The banana-shaped molecules fit to the bend structure and the FE polarization points to the bend centre. In the splayed structure the molecules are slightly turned and the average polarization is opposite to the splay centre position.

4 Conclusions

In this paper, the statistical theory was used to study the dependence between the microscopic and macroscopic parameters of nematic liquid crystals. The temperature dependence of the order parameters, the FE coefficients, and the elastic constants was obtained for the two systems. For the wedge-shaped molecules the bend coefficient e_3 is almost constant whereas the splay coefficient e_1 is changing monotonically. For the banana-shaped molecules the splay coefficient e_1 is almost constant whereas the bend coefficient e_3 is changing monotonically. In both cases the FE coefficients are proportional to the molecule dipole moment component, parallel to the molecule symmetry axis. This is the long axis of the wedge-shaped molecules and the short axis of the banana-shaped molecules. It results from the symmetries of the interactions and of the Mayer function. In other theories, where the interactions are not explicitly used or they are more complicated, the dependence on the all dipole moment components is present. The results are consistent with the microscopic pictures from the paper by Meyer but two additional situations were taken into account, the splayed phase with banana-shaped molecules and the bend phase with wedge-shaped molecules.

At present stage, the qualitative comparison between the theory and the experiment is very difficult. The experimental data on the FE coefficients are still scarce and sometimes contradictory [16]. On the other hand, a nontrivial dependence on the details of the chemical structure was shown [17]. A small chemical modification of the molecule can generate significant change of the flexoelectricity. Thus, we would like to give only the estimates assuming typical values of the model parameters. If we assume the molecular length $\sigma_0 = 1nm$, the interaction energy $\epsilon = 0.1eV$, and the electric dipole moment $\mu = 1D$, then we can estimate the values of the FE coefficients $\mu/\sigma_0^2 = 3.3pC/m$, the elastic constants $\epsilon/\sigma_0 = 16pN$, and the temperature $\epsilon/k_B = 1160K$ (it is three/four times larger than the typical isotropic-nematic transition temperature).

The theory should be improved in order to describe exactly real systems. For the distance σ , the general expansion proposed by Blum and Torruella [18] can be applied in order to describe molecular shapes better. The Meyer function f_{12} used in the low density limit can be replaced with the direct correlation function c_{12} from the Percus-Yevick approximation. In many cases, liquid crystals are mixtures of different substances or different conformers and it should be taken into account. Finally, it is possible to consider the

FE effect in the biaxial nematic phase although this phase is still very rare.

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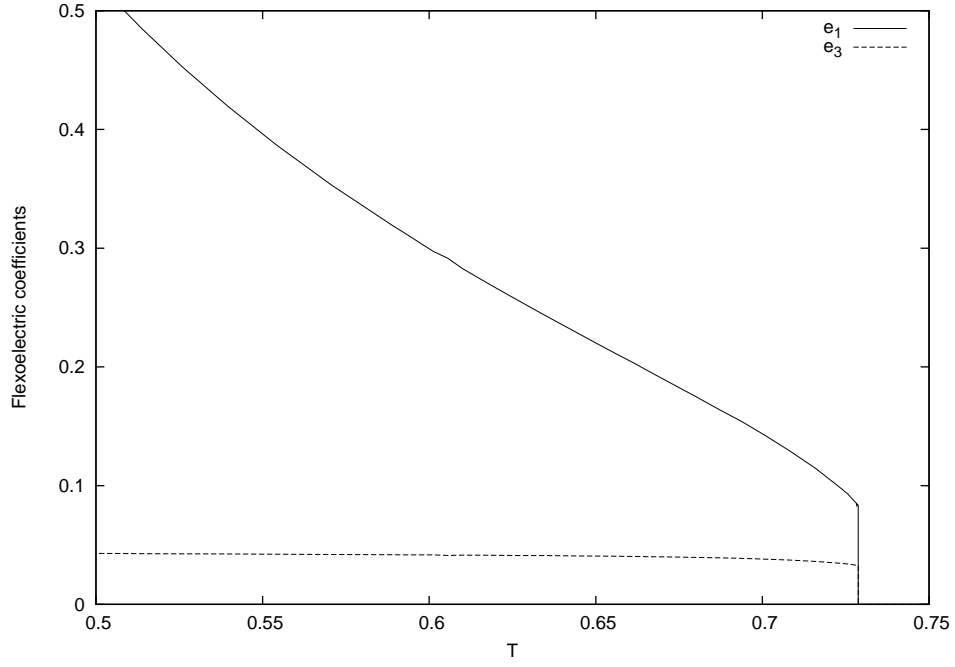


Figure 1: The temperature dependence of the flexoelectric coefficients e_i expressed in μ_3/σ_0^2 in the case of wedge-shaped molecules. The temperature T is expressed in ϵ/k_B . The $I - N$ transition is at $T_C = 0.7287$.

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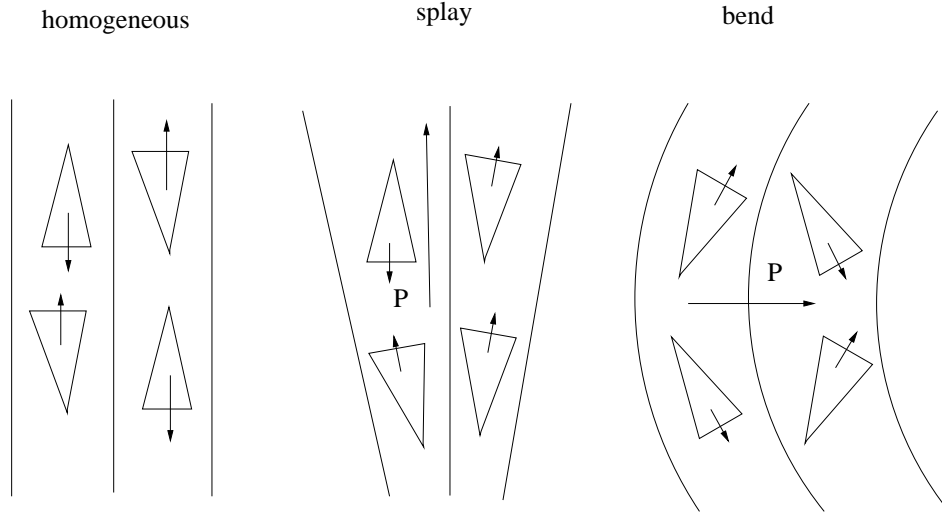


Figure 2: The homogeneous, the splay, and the bend phases of wedge-shaped molecules. The solid lines denote the local direction \vec{N} . The z axis is the symmetry axis of the homogeneous nematic phase. In the splay phase there is an excess of molecules pointing down to the splay origin. In the bend phase there is an excess of molecules pointing to the left whereas the bend center is on the right.

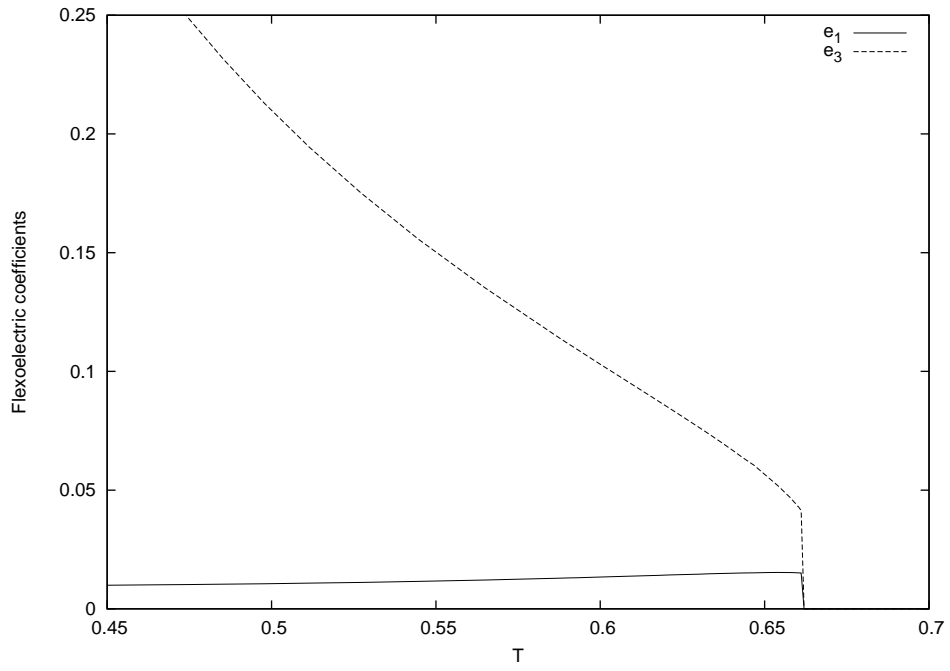


Figure 3: The temperature dependence of the flexoelectric coefficients e_i expressed in μ_1/σ_0^2 in the case of banana-shaped molecules. The temperature T is expressed in ϵ/k_B . The $I - N$ transition is at $T_C = 0.6611$.

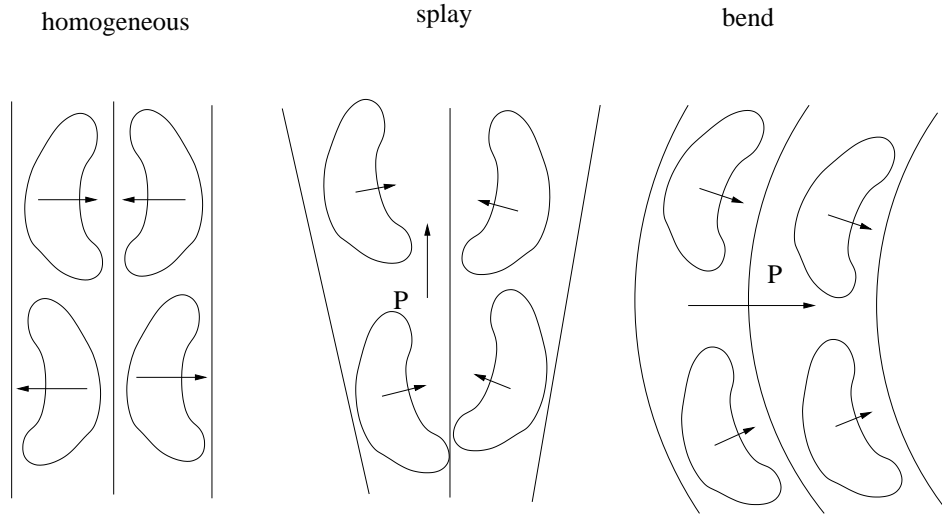


Figure 4: The homogeneous, the splay, and the bend phases of banana-shaped molecules. The solid lines denote the local direction \vec{N} . The z axis is the symmetry axis of the homogeneous nematic phase. In the splay phase, molecules are slightly turned and the average polarization direction is opposite to the splay origin. In the bend phase, the molecule dipole moments point to the bend center on the right.